

Thermodynamics of a quantized electromagnetic field in rectangular cavities with perfectly conducting walls

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Abstract

The thermodynamical properties of a quantized electromagnetic field inside a box with perfectly conducting walls are studied using a regularization scheme that permits to obtain finite expressions for the thermodynamic potentials. The source of ultraviolet divergences is directly isolated in the expression for the density of modes, and the logarithmic infrared divergences are regularized imposing the uniqueness of vacuum and, consequently, the vanishing of the entropy in the limit of zero temperature. We thus obtain corrections to the Casimir energy and pressures, and to the specific heat that are due to temperature effects; these results suggest effects that could be tested experimentally.

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I. INTRODUCTION

The theory of blackbody radiation in cavities has played a decisive role in the development of quantum physics. In particular, the existence of a zero-point energy [1] with measurable physical effects, as predicted by Casimir in 1948 [2], followed from its consistency. It is now well established that the fluctuations of the quantum vacuum induce an attractive force of magnitude (per unit area) $\pi^2\hbar c/240L^4$ between two perfectly-conducting parallel plates separated a distance L . The physical importance of the Casimir effect prompted an extensive investigation of the fundamental properties of quantum and thermal fluctuations for a large variety of systems with particular dielectric and geometric features[3, 4, 5]. Nevertheless, a complete self-consistent theory of quantum fluctuations in closed cavities is far from being achieved due to the lack of a clear and well established regularization scheme.

In the simplest case of an ideal conducting parallel-plate configuration at finite temperature, relevant thermodynamical quantities such as entropy, internal and free energies, and pressure forces have been calculated by many authors following different lines [4, 5, 6, 7, 8]. In a pioneering work based on general symmetry considerations, Brown and Maclay [5] analyzed the structure of the electromagnetic stress-energy tensor $T^{\mu\nu}$ for two parallel plates immersed in a thermal bath at a temperature T . They found that this tensor can be written as a sum of three terms:

$$T^{\mu\nu} = T_{0;L}^{\mu\nu} + T_{T;\infty}^{\mu\nu} + T_{T;L}^{\mu\nu}, \quad (1)$$

where the first term represents the zero-point Casimir stress tensor for a plate separation L , the second is due to the black body radiation between widely separated plates, and the third term is a correction that vanishes in the limits $T \rightarrow 0$ and $L \rightarrow \infty$. The resulting energy density coincides with the standard Stefan-Boltzmann expression, $E/V = T_{T;\infty}^{00} = (\pi^2/15\hbar^3c^3)(k_B T)^4$, but there is also a contribution due to boundary effects in the limit $T \rightarrow \infty$: the pressure at the plates deviates from the standard blackbody pressure by a term that increases linearly with the temperature. This additional term is independent of \hbar [5]; in fact, Boyer [9] also derived it within a purely classical formalism, and Mehra [4], and Feinberg *et al.* [7] obtained identical results. This linear term has also been found for other geometries and materials [10, 11].

There are some controversial issues regarding the Casimir forces between dielectric parallel plates. For instance, the Lifshitz formula [12] that follows from a direct application of

Matsubara's frequencies formula is ambiguous in the infrared regime. The fundamental issue seems to be whether the transverse electric (TE) component of the electromagnetic field contributes to the Casimir force in that regime. The theoretical answer depends on the model used to characterize the dielectric response of the material: at low frequencies, the TE mode vanishes if the Drude model for the dielectric function is used [13], but this is not the case of the plasma model [14]. According to the first approach, there must be a large thermal correction to the Casimir force between plates with a separation of one micrometer or larger, but no such effect has been observed in experiments [15, 16]. Moreover, Bezerra *et al.* [17] have shown that using the Drude model, the entropy turns out to be finite at zero temperature and depends on the parameters of the system, thus violating the third law of thermodynamics; these authors proposed to solve the problem with the plasma model and the Leontovich surface impedance approach, but the applicability of this scheme has been questioned by others [18, 19, 20]. Still other authors [16, 20, 21] have concluded that some of the discrepancies are due to the fact that, in the low frequency regime, the atomic nature of the material invalidates the use of dielectric functions that characterize bulk properties.

The problem becomes considerably more complicated beyond the parallel plates configuration. In their pioneering work, Case and Chiu [22] used the fluctuation-dissipation theorem to calculate the mean internal energy inside a perfectly conducting cavity filled with a dielectric dispersive medium at finite temperature. For an empty cubic cavity, they obtained an expression for the internal energy per unit volume similar to Eq.(1), and they also found a deviation from the Stefan-Boltzmann law at low temperatures. However, Case and Chiu did not calculate other thermodynamic potentials that also characterize the system.

In a later work, Ambjorn and Wolfram [6] studied the general problem of the constrained vacuum fluctuations of *scalar* fields in D-dimensional Euclidean spaces, subject to either Dirichlet or Neumann boundary conditions along P orthogonal directions; they calculated the partition function of such a configuration with a dimensional regularization technique. However, the resulting partition function for a completely closed cavity ($D = P$) turned out to be divergent, as well as thermodynamic quantities such as the free energy and the entropy. Ambjorn and Wolfram claimed that these divergences could be removed introducing two further regularization schemes, valid at low and high temperatures separately, but they gave no explicit expressions for the finite thermodynamic potentials that may be valid at *all* temperatures. A similar problem also arises when dealing with *electromagnetic* fluctuations

in rectangular closed cavities, as shown by Santos and Tort [23] who studied the asymptotic behavior of the free energy at low and high temperatures using a duality inversion formula. Such a duality symmetry was formerly discovered by Brown and Maclay for the parallel plate configuration [5] and studied by Ravndal and Tollefsen [24]. More recent works along these lines are due to Inui [25] and Cheng [26]. However, none of these authors report the free energy of the EM field in a closed and finite form that could be valid for all temperatures and box geometries. As a consequence, no quantitative predictions for temperature corrections to the Casimir pressures can be deduced from these works.

The aim of the present paper is to study the thermal effects of a quantum electromagnetic field in closed rectangular cavities with perfectly conducting walls. For this purpose, we propose a regularization scheme that permits to calculate the thermodynamical variables and obtain finite results that can be eventually tested in laboratories. The analogous problem in the zero-temperature case has been addressed in several previous works [6, 27, 28, 29], the main results being that the Casimir energy and pressures on the cavity plates depend strongly on the geometry (they can even change sign according to the relative ratios of the faces). In general, the Casimir pressures produce instabilities and, in the particular case of a cube, the forces acting on its faces are repulsive[28]. In the present paper we generalize the previous results to include a thermal bath in the configuration. In Section 2, the regularization is achieved using a particular representation of the EM mode density that permits to isolate the contributions of ultraviolet divergences (arising from zero-point fluctuations, to the internal and free energies). For this purpose, we first isolate the contribution to the mode density in a large cavity, as given by Weyl's asymptotic expression, including correction terms proportional to the edges of the configuration. Next, the infrared divergences are regularized by imposing the uniqueness of the vacuum state, *i.e.* the state without photons of any frequency, in such a way that the entropy of the system at zero temperature is zero by construction. The regularized free energy is then used to calculate the pressures, which are physical observable quantities in experiments. In Section. 3, our results are compared with other approaches in order to elucidate the origin of the difficulties arising in the problem of quantum and thermal fluctuations in rectangular cavities.

II. THERMODYNAMIC VARIABLES

For any given field at thermal equilibrium with its surroundings, the contribution to the free energy of a mode of frequency $\omega_{\mathbf{k}}$ is

$$F(\omega_{\mathbf{k}}) = T \ln(1 - e^{-\hbar\omega_{\mathbf{k}}/T}) + \frac{1}{2}\hbar\omega_{\mathbf{k}}, \quad (2)$$

in standard notation, where the second term is the contribution of the zero-point field (from now on, we set $k_B = 1$). The total free energy is a sum over the set of modes:

$$F = \int \rho(\omega_{\mathbf{k}})F(\omega_{\mathbf{k}})d\omega_{\mathbf{k}}, \quad (3)$$

where $\rho(\omega_{\mathbf{k}})$ is the density of modes.

If we consider a rectangular cavity with sizes a_k ($k = 1, 2, 3$) made of an idealized perfect conducting material, the boundary conditions imply the discretization of the frequencies in the box:

$$\omega_{\mathbf{n}} = \pi c \sqrt{\left(\frac{n_1}{a_1}\right)^2 + \left(\frac{n_2}{a_2}\right)^2 + \left(\frac{n_3}{a_3}\right)^2}. \quad (4)$$

The density of modes has the form [22, 23, 28]

$$\rho(\omega) = \frac{1}{4} \sum'_{\mathbf{n}} \delta(\omega - \omega_{\mathbf{n}})(1 - \delta_{n_1 0} \delta_{n_2 0} - \delta_{n_2 0} \delta_{n_3 0} - \delta_{n_3 0} \delta_{n_1 0}), \quad (5)$$

where the prime in the summation indicates that the term with all three indices $n_i = 0$ is to be excluded. This particular form of $\rho(\omega)$ reflects the fact that the normal (parallel) components of the magnetic (electric) field vanish on the walls of the cavity, and that the electromagnetic field admits two polarization states represented by transverse electric (TE) and transverse magnetic (TM) modes. These modes may be derived from massless scalar Hertz potentials that satisfy mixed combinations of Dirichlet or Neumann boundary conditions on the cavity plates [28, 31].

As shown in Ref. [28], ultraviolet divergences of the zero-point energy can be isolated. For this purpose, the spectral density is written in terms of a summation involving the variable

$$u_{\mathbf{n}} = \frac{2}{c} \left[(n_1 a_1)^2 + (n_2 a_2)^2 + (n_3 a_3)^2 \right]^{1/2}, \quad (6)$$

which is conjugate to the frequency variable ω . As shown in Ref. [28], it is convenient to separate the density of modes into two parts:

$$\rho(\omega) = \rho^{\infty}(\omega) + \Delta\rho(\omega), \quad (7)$$

where the first term is

$$\rho^\infty(\omega) = \frac{V}{\pi^2 c^3} \omega^2 - \frac{1}{2\pi c} (a_1 + a_2 + a_3) , \quad (8)$$

and the second term can be written in the form

$$\begin{aligned} \Delta\rho(\omega) &= \frac{V}{\pi^2 c^3} \sum_{\mathbf{n}=-\infty}^{\infty} \left[\frac{\omega \sin(\omega u_{\mathbf{n}})}{u_{\mathbf{n}}} - \frac{a_1}{2\pi c} \sum_{n=-\infty}^{\infty} \right] \cos(\omega u_{n00}) \\ &\quad - \frac{a_2}{2\pi c} \sum_{n=-\infty}^{\infty} \cos(\omega u_{0n0}) - \frac{a_3}{2\pi c} \sum_{n=-\infty}^{\infty} \cos(\omega u_{00n}) . \end{aligned} \quad (9)$$

The above relations are valid for all values of $\omega \neq 0$.

The variable $cu_{\mathbf{n}}$ in the above formula can be interpreted as the position of the image charges that generate the field correlation functions with the appropriate boundary conditions on the conducting walls [28, 30]. Moreover, since these variables are conjugate to the frequency, lower values of the integer n_i 's in $u_{\mathbf{n}}$ correspond to higher values of the frequency, and vice versa. Notice also that Eq. (9) is not well defined for $\omega = 0$ because the terms related to edges diverge, while in the original expression for $\rho(\omega)$, Eq. (5), the term with $\omega = 0$ is absent.

The spectral density $\rho^\infty(\omega)$ prevails in the limit $a_i \rightarrow \infty$, but it is not identical to the density of modes in free space because the edge terms are important even in this limit. However, just for simplicity, we shall call it “free” or “blackbody” density. The use of $\Delta\rho(\omega)$ instead of the full density of states $\rho(\omega)$ for evaluating an extensive variable is equivalent to calculating the *difference* between the values of that variable in bounded and in “free” space.

The contribution of the zero-point field to either the free or the internal energy associated to $\rho^\infty(\omega)$ is always divergent. However, the temperature dependent part of the free energy that corresponds to the blackbody radiation is perfectly finite and is given by

$$\begin{aligned} F_{BB}^\infty &\equiv T \int_0^\infty \rho^\infty(\omega) \log(1 - e^{-\hbar\omega/T}) d\omega \\ &= -\frac{\pi^2}{45\hbar^3 c^3} V T^4 - \frac{\pi^2}{12\hbar c} (a_1 + a_2 + a_3) T^2 . \end{aligned} \quad (10)$$

The first term, proportional to the volume of the box, is the usual text-book formula; the second term is the contribution of the cavity edges to the free energy [32]. It is easy to see from a dimensional analysis that any contribution to the free energy proportional to

the surface of the walls $a_i a_j$ should be proportional to T^3 , and similarly a contribution related to the vertices should be proportional to T and independent of the parameters a_i . As mentioned above, contributions to the spectral density from faces and vertices of the cavity do not appear due to a cancellation of the corresponding TE and TM modes [28, 32]. In any case, a correction of the Stefan-Boltzmann law, possibly as the one given by Eq. (10), has been observed during the development of masers technology[33].

The contribution of the spectral density $\Delta\rho(\omega)$ to the zero-point free or internal energy is the Casimir term

$$\begin{aligned}\Delta E_0 &= \frac{\hbar}{2} \int_0^\infty \omega \Delta\rho(\omega) d\omega \\ &= -\frac{\hbar}{\pi^2 c^3} V \sum'_{\mathbf{n}} \frac{1}{u_{\mathbf{n}}^4} \\ &\quad + \frac{\hbar}{4\pi c} a_1 \sum'_n \frac{1}{u_{n00}^2} + \frac{\hbar}{4\pi c} a_2 \sum'_n \frac{1}{u_{0n0}^2} + \frac{\hbar}{4\pi c} a_3 \sum'_n \frac{1}{u_{00n}^2}.\end{aligned}\quad (11)$$

The thermal part of the free energy calculated with $\Delta\rho(\omega)$ turns out to be free of ultraviolet divergences. However, some of the integrals involved do not have a unique interpretation as shown in the Appendix. In fact,

$$\begin{aligned}\Delta F &= \Delta E_0 + \frac{\pi^2}{2\hbar^3 c^3} V T^4 \sum'_{\mathbf{n}} h_V(v_{\mathbf{n}}) \\ &\quad + \frac{\pi}{4\hbar c} T^2 \sum_n [a_1 f_E(v_{n00}) + a_2 f_E(v_{0n0}) + a_3 f_E(v_{00n})],\end{aligned}\quad (12)$$

where we have defined

$$\begin{aligned}f_{V,E}(v) &= \frac{1}{v} (g(v) - K_{V,E}(v)) , \\ h_{V,E}(v) &= h(v) + \frac{1}{v^3} K_{V,E}(v) , \\ g(v) &= \coth(v) - \frac{1}{v} , \\ h(v) &= \frac{1}{v} \frac{d}{dv} \left(\frac{1}{v} g(v) \right)\end{aligned}\quad (13)$$

as functions of the dimensionless variable

$$v_{\mathbf{n}} = \frac{\pi T}{\hbar} u_{\mathbf{n}}$$

(at room temperature $k_B T \sim 2.6 \times 10^{-2}$ eV, and this implies that $\hbar c / \pi k_B T \sim 3 \mu\text{m}$). $K_V(v)$ and $K_E(v)$ are trichotomic functions of v that can take only the values ± 1 and 0, depending

on the contour of integration selected to evaluate the integrals appearing in the volume and edge parts, respectively, of the free energy ΔF . Notice that in the limit $T \rightarrow 0$, the free energy ΔF is equal to the internal energy ΔE_0 independently of the value of K .

In general, given an integral expression for a physical variable, the selection of an integration path corresponds to a particular boundary condition for that variable. In the following, we shall impose the limiting condition

$$\left. \frac{\partial F}{\partial T} \right|_{T \rightarrow 0^+} = 0 , \quad (14)$$

in order to select an appropriate integration path for a given value of $v_{\mathbf{n}}$. The entropy \mathcal{S} of the system being

$$\mathcal{S} \equiv -\frac{\partial F}{\partial T} = \mathcal{S}_{BB}^\infty + \Delta\mathcal{S} , \quad (15)$$

Eq. (14) implies the uniqueness of the EM vacuum. The blackbody contribution to the entropy is

$$\mathcal{S}_{BB}^\infty = \frac{4\pi^2}{45\hbar^3 c^3} V T^3 + \frac{\pi^2}{6\hbar c} (a_1 + a_2 + a_3) T , \quad (16)$$

and using the integrals given in the Appendix, the remaining part of the entropy can be written as

$$\begin{aligned} \Delta\mathcal{S} = & -\frac{\pi^2 V T^3}{2\hbar^3 c^3} \sum'_{n_i} \left[v_{\mathbf{n}} h'(v_{\mathbf{n}}) - \frac{3}{v_{\mathbf{n}}^3} K_V(v_{\mathbf{n}}) + 4h_V(v_{\mathbf{n}}) \right] \\ & - \frac{\pi a_1 T}{4\hbar c} \sum'_n \left[2f_E(v_{n00}) + v_{n00}^2 h_E(v_{n00}) \right] \\ & - \frac{\pi a_2 T}{4\hbar c} \sum'_n \left[2f_E(v_{0n0}) + v_{0n0}^2 h_E(v_{0n0}) \right] \\ & - \frac{\pi a_3 T}{4\hbar c} \sum'_n \left[2f_E(v_{00n}) + v_{00n}^2 h_E(v_{00n}) \right]. \end{aligned} \quad (17)$$

In order to evaluate the limit $T \rightarrow 0$ of the above formulas, the summation over discrete indices can be replaced by an integration over a continuous dummy variable v :

$$\mathcal{S} \rightarrow -\frac{1}{4} \int_0^\infty dv \left[v^2 [vh'(v) - \frac{3}{v^3} K_V(v) + 4h_V(v)] + 6f_E(v) + 3h_E(v) \right]. \quad (18)$$

This expression is independent of the geometric parameters a_i as expected from Nernst's third law of thermodynamics. The direct evaluation of these integrals gives the result

$$\begin{aligned} \mathcal{S} \rightarrow & -\frac{1}{4} \int_0^\infty dv \frac{1}{v} \left(\coth(v) - K_V(v) - \frac{1}{v} \right) \\ & - \frac{3}{4} \left[1 + \int_0^\infty dv \frac{1}{v} \left(\coth(v) - K_E(v) - \frac{1}{v} \right) \right], \end{aligned} \quad (19)$$

where the first term comes from the contribution of the volume terms, and the second from the edge terms. Now, if $K(v)$ is taken strictly either as 0, or as 1 or as -1 for any value of v , the entropy at zero temperature will not be zero; even worse, it will clearly diverge. If $K = 0$, the integrands would be regular at $v = 0$, while the edge and volume integrals would have a logarithmic divergence. On the other hand, if K equals 1 or -1, the integrand would not be regular at $v = 0$ and the integrals would diverge. Thus, the simplest way of keeping a bounded value for the entropy is to choose $K = 0$ for $v < v_0$ and $K = 1$ for larger values of v , with v_0 to be determined. Accordingly, we define the function

$$G(v_0) = \int_0^{v_0} dv \frac{1}{v} \left(\coth(v) - \frac{1}{v} \right) + \int_{v_0}^{\infty} dv \frac{1}{v} \left(\coth(v) - \frac{1}{v} - 1 \right), \quad (20)$$

and choose a value of v_0 in such a way that the entropy does take the value zero at $T = 0$. A plot of $G(v_0)$ is shown in Fig. 1; it turns out to be a increasing function of v_0 , such that $G(v_V) = 0$ and $G(v_E) = -1$ for $v_V = 1.763876988$ and $v_E = 0.64889408$ (with ten significant figures).

Thus choosing $K_{V,E} = \Theta(v - v_{V,E})$, where Θ is the standard step function, we guarantee that ΔF satisfy the boundary condition Eq. (14) and that a finite regularized value of the thermodynamic variables ΔF and ΔS is obtained.

At this point, we recall that the spectral density given by Eq. (9) is not valid for $\omega = 0$; however, if this equation is taken as it stands for all values of ω , it includes a term proportional to $\delta(\omega)$. It is precisely such a term that gives rise to the extra factor $3/4$ appearing in the contributions of the edges to the entropy at zero temperature in Eq. (19). This unphysical contribution to the entropy is properly removed by the selection of v_E .

From a physical point of view, it is not possible in general to distinguish between processes that differ from each other by the emission of a certain number of low energy photons with $\omega \rightarrow 0$. In free space, this is true for a continuum, but in a closed box, the values of $v_{V,E}$ are the ones that define which photons should be taken as being of low energy; namely,

$$v_n > v_V \Leftrightarrow k_B T > \frac{\hbar c v_V}{u_n \pi}, \quad (21)$$

and this condition determines whether the photons contribute to the counting of microstates. That is to say, the uniqueness of the vacuum determines which modes are to be considered as infrared.

Given S and F , the expression for the internal energy can be directly calculated as

$$E(T) = E_{BB}(T) + \Delta E(T) ,$$

where

$$E_{BB}^\infty = \frac{\pi^2}{15\hbar^3 c^3} VT^4 + \frac{\pi^2}{12\hbar c}(a_1 + a_2 + a_3)T^2$$

and

$$\begin{aligned} \Delta E(T) &= \Delta F + T\Delta S \\ &= \Delta E_0 - \frac{\pi^2}{2\hbar^3 c^3} VT^4 \sum_{a_1 a_2 a_3} \left[\frac{1}{v_{lnm}} g''(v_{lnm}) \right. \\ &\quad \left. - \frac{\pi}{4\hbar c} T^2 \sum_n \left[a_1 g'(v_{n00}) + a_2 g'(v_{0n0}) + a_3 g'(v_{00n}) \right] \right]. \end{aligned} \quad (22)$$

Notice that $\Delta E(T)$ does not depend on the value of K . In fact, this expression can be obtained directly from the spectral density without any explicit calculation of ΔS and ΔF . The regular behavior of ΔE is the reason why previous authors have restricted their calculations to this particular thermodynamical variable [22].

The behavior of the total entropy and the difference between its “free space” and bounded space values, is shown in Fig. 2, together with the free and internal energies. Three particular configurations were considered for the numerical calculations: the cases of a “pizza box”, $a_2 = a_3 = 100a_1$; a cube, $a_1 = a_2 = a_3$; and a wave-guide configuration, $a_2 = a_3 = a_1/10$. Some common features are worth noticing: (i) the total entropy S and the relative entropy ΔS are zero at $T = 0$, as it should be by construction; (ii) the total entropy is always positive; (iii) the relative entropy may take negative values and, accordingly, heat may be released by the system when going from free space to a bounded configuration; (iv) the entropy and free energy of the system are discontinuous functions of the temperature; (v) the free and internal energies equal the Casimir energy at $T = 0$; (vi) all relative thermodynamic variables tend to zero as $T \rightarrow \infty$.

The case $a_2 = a_3 = 100a_1$ is similar to the widely studied parallel plates configuration; it must be realized, however, that there is a qualitative difference between the two configurations: in closed rectangular boxes, all frequencies are discrete and **no** zero frequency electromagnetic modes are allowed, whereas parallel plates admits a continuous range of frequencies and the existence of either *TE* and *TM* of *zero* frequency is not excluded in principle[20]. The presence of such modes significantly alters the behavior of the free and internal energies at high temperatures and introduce terms that increase linearly with temperature [5, 9, 20]. Our calculations show that for a closed rectangular cavity, such linear terms are absent and that, moreover, all the effects associated to the discrete density of modes $\Delta\rho(\omega)$ tend to

disappear as the temperature increases. The case of a cube, $a_1 = a_2 = a_3$, is particularly interesting since its Casimir energy is positive; in this case, the difference between the free and bounded internal energy ΔE is a decreasing function of the temperature. In the case $a_1 = a_2 = a_3/10$, the cavity is similar to a waveguide and discontinuities of F and S persist at higher temperatures.

Once a regularized expression for the thermodynamic potentials has been obtained, other relevant physical variables can be directly calculated. For instance, the specific heat C_V for a given geometry,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \quad (23)$$

is clearly a continuous function of T . For a cube, it turns out that the presence of the boundaries reduces the specific heat C_V with respect to the case with boundaries at infinity, while the opposite effect occurs for the “pizza box”, $a_1 \ll a_2 = a_3$. As a general feature, C_V decreases at very low temperatures with respect to the free space configuration, but increases at moderate temperatures.

The pressure on wall 1 of area $a_2 a_3$ is given by

$$P_1 = -\frac{1}{a_2 a_3} \left(\frac{\partial F}{\partial a_1} \right)_T , \quad (24)$$

with similar expressions for P_2 and P_3 . A straightforward calculation shows that, as expected, the equation of state

$$E = (P_1 + P_2 + P_3)V \quad (25)$$

is satisfied. For a cube $P_1 = P_2 = P_3 = E/3V$ and the pressure is a continuous functions of T . For other configurations, the regularized expression of F leads to discontinuities of the pressures at the walls at low temperature. This can be seen in Fig. 3, where a plot is shown of the total pressure at walls 1 and 3 for “waveguide” and “pizza box” configurations. It is worth recalling that the pressure is the physical variable most accessible to experimental verification.

A common feature of some thermodynamic variables for all configurations is the appearance of discontinuities as the temperature varies. These discontinuities are due to the different weights that the EM modes acquire as the temperature increases.

III. OTHER APPROACHES

In this section we compare our results with those reported in the literature for the same or similar systems. For this purpose, it is convenient to use the formula

$$\coth \pi x - \frac{1}{\pi x} = \frac{2x}{\pi} \sum_{k=1}^{\infty} \frac{1}{x^2 + k^2} \quad (26)$$

and write the regularized free energy in the form

$$\begin{aligned} \Delta F = \Delta E_0 + \Delta F_M + \frac{V}{2\pi c^3} T \sum_{|v_{\mathbf{n}}| > v_V} \frac{1}{u_{\mathbf{n}}^3} \\ - \frac{\pi}{4} T \left[\sum_{v_{n00} > v_E} \frac{1}{n} + \sum_{v_{0n0} > v_E} \frac{1}{n} + \sum_{v_{00n} > v_E} \frac{1}{n} \right], \end{aligned} \quad (27)$$

where ΔF_M is the free energy that follows directly from the Matsubara formalism, see *e. g.* Santos and Tort[23]. It can be obtained in our own formalism using $\Delta\rho$ with the integration paths so chosen that K_V and K_E are taken as zero for every v_{nlm} . Explicitly:

$$\begin{aligned} \Delta F_M = - \frac{2V\hbar}{\pi c^3} \sum'_{\mathbf{n}} \sum_{k=1}^{\infty} \frac{1}{[(k\hbar/T)^2 + u_{\mathbf{n}}^2]^2} + \frac{\hbar a_1}{c} \sum_{n,k=1}^{\infty} \frac{1}{(k\hbar/T)^2 + u_{n00}^2} \\ + \frac{\hbar a_2}{c} \sum_{n,k=1}^{\infty} \frac{1}{(k\hbar/T)^2 + u_{0n0}^2} + \frac{\hbar a_3}{c} \sum_{n,k=1}^{\infty} \frac{1}{(k\hbar/T)^2 + u_{00n}^2}. \end{aligned} \quad (28)$$

Notice that this expression has a logarithmic divergence and, consequently, it precludes any practical calculation of physical quantities. The analogue of ΔF_M for a massless scalar field was reported in Ref. [6], where, as mentioned above in the Introduction, the problem of the divergence was stated but no explicit finite expression for the free energy, valid at all temperatures, was given.

From the explicit form of the terms that depend on $K_{V,E}(v)$ in Eq. (12), it can be seen that they have a quantum origin: although each term in the summation is independent of \hbar , the selection of the integers n_i that contribute to the summation depends on \hbar . Indeed, Santos and Tort [23] have shown that the free energy of the EM field calculated using the Z -function regularization technique is identical with ΔF_M up to a term $T \ln(\mu/\sqrt{2\pi} T)$, where μ is a scale factor. Santos and Tort choose $\mu = \sqrt{2\pi} T$, whereas in our regularization scheme

$$\mu = \sqrt{2\pi} T \exp \left\{ \frac{V}{2\pi c^3} \sum_{|v_{\mathbf{n}}| > v_V} \frac{1}{u_{\mathbf{n}}^3} - \frac{\pi}{4} \left[\sum_{v_{n00} > v_E} \frac{1}{n} + \sum_{v_{0n0} > v_E} \frac{1}{n} + \sum_{v_{00n} > v_E} \frac{1}{n} \right] \right\} \quad (29)$$

is the scale factor.

Since it is well known that most difficulties with the quantization of the electromagnetic field are related to the fact that it is a massless field, the origin of our divergence problem can also be clarified by assigning an effective mass m_γ to the photon. For a massive field, the volumetric contribution to ΔF_M must be changed to [6]:

$$\Delta F_M(m_\gamma) = -\frac{Vm_\gamma^2 c}{4\pi^2 \hbar} \sum'_{\mathbf{n}} \sum_{k=1}^{\infty} \frac{K_2\left((m_\gamma c^2/2\hbar)\left[(\hbar k/T)^2 + u_{\mathbf{n}}^2\right]^{1/2}\right)}{(\hbar k/T)^2 + u_{\mathbf{n}}^2}, \quad (30)$$

where K_2 is the associated Bessel function. The limit of low temperature, $T \rightarrow 0$, of this expression can be calculated as a continuous integral over variables n_i , with the result

$$\Delta F_M(m_\gamma) \simeq -T \ln \left(1 - e^{-m_\gamma c^2/2T} \right), \quad (31)$$

from where the following contribution to the entropy is obtained:

$$\Delta S_M(m_\gamma) = -\frac{\partial F_{BB}}{\partial T} = \ln \left(1 - e^{-m_\gamma c^2/2T} \right) + \frac{m_\gamma c^2}{2T} \frac{1}{e^{m_\gamma c^2/2T} - 1}, \quad (32)$$

which is finite and does tend to zero in the limit of low temperature. Clearly this limit is to be understood in the sense that $T \ll m_\gamma c^2$. Had we taken $m_\gamma = 0$ from the beginning, the entropy would not be finite; thus the origin of the divergence can be traced back to the fact that, since the photon is massless, there is no natural energy for the temperature to be compared with; this seems to be the origin of the difficulties with the definition of entropy in closed rectangular cavities. In principle, one could use Eq. (30) to calculate the thermodynamic variables and take the limit of zero mass only at the end, but this procedure is not useful for practical computations; as far as we know, no expression for the regularized quantities in closed form has been obtained in this way.

IV. SUMMARY AND CONCLUSIONS

In this paper we have obtained fully regularized expressions for the thermodynamic variables associated to the electromagnetic field inside a rectangular box with perfect conducting walls. The regularization procedure we have used is based on the condition that the entropy be zero at $T = 0$, which is equivalent to imposing the uniqueness of EM vacuum. In this way, we have been able to calculate thermodynamical quantities that could be tested experimentally.

In general, infrared divergences in these type of calculations are due to the possible emission and absorption of an indefinite number of soft photons. However, in a closed rectangular cavity of maximum size L , the frequencies are discrete and there must be a lower bound to the frequency, $\omega_{min} = c/2L$, such that the limit $\omega \rightarrow 0$ is never achieved in the system. According to our analysis, this seems to be the origin of the difficulties in the infrared limit. Thus special care must be taken in counting the different microstates in the evaluation of the free energy: specifically, it is necessary to impose the uniqueness of the state without photons of any allowed frequency. Otherwise, the entropy is not well defined at zero temperature.

In the regularization scheme we propose, we have taken the above facts into account using a cut-off procedure. According to quantum statistics, the cut-off values v_V and v_E can be interpreted as parameters that define which EM modes are compatible with the macrostate of a given configuration, that is, those that must be properly counted at low temperatures. In particular, it turns out that the cut-off related to the volume and the edges of the configuration are different: $v_V \neq v_E$.

The introduction of cut-off terms is also related to the fact that all energy fluctuations induced by the thermal bath must be larger than the quantum fluctuations. Actually, this is the meaning of the important inequality (21). On the other hand, if the photons had an effective mass $m_\gamma \sim \hbar/Lc$, no cut-off would be necessary.

The discontinuities exhibited by the free energy and the entropy, associated with the modes that fit into the configuration as the temperature varies, are some of the most striking predictions of our calculations. However, they could be due to an excessive idealization of the system under study, namely, a perfectly conducting cavity at thermal equilibrium with its surroundings. It may happen that for a dielectric closed box such discontinuities are softened, but traces of them could be present in experiments.

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Appendix

A basic integral to be evaluated is:

$$\begin{aligned}
& -\frac{u}{\beta\hbar} \int_0^\infty d\omega \cos(u\omega) \ln(1 - e^{-\beta\hbar\omega}) \\
&= \int_0^\infty d\omega \frac{\sin(u\omega)}{e^{\beta\hbar\omega} - 1} \\
&= \frac{1}{4} \int_{-\infty}^\infty d\omega \sin(u\omega) \coth(\beta\hbar\omega/2) - \frac{1}{2} \int_0^\infty d\omega \sin(u\omega) \\
&= \frac{\pi}{2\beta\hbar} \left[\coth\left(\frac{\pi u}{\beta\hbar}\right) - K \right] - \frac{1}{2} \mathcal{P} \frac{1}{u}
\end{aligned} \tag{33}$$

(for $u \neq 0$). The value of this integral depends on the integration path used to circumvent the pole at $\omega = 0$. For a given $u > 0$, one finds that $K = \pm 1$ if the path circumvents the singularity over (under) the real axis, and $K = 0$ if the principal value of the integral is taken.

The other basic integral is

$$\begin{aligned}
& -\frac{u}{\beta\hbar} \int_0^\infty d\omega \omega \sin(u\omega) \ln(1 - e^{-\beta\hbar\omega}) \\
&= - \int_0^\infty d\omega \omega \frac{\cos(u\omega)}{e^{\beta\hbar\omega} - 1} + \frac{1}{u} \int_0^\infty d\omega \frac{\sin(u\omega)}{e^{\beta\hbar\omega} - 1},
\end{aligned} \tag{34}$$

with

$$\begin{aligned}
\int_0^\infty d\omega \omega \frac{\cos(u\omega)}{e^{\beta\hbar\omega} - 1} &= \frac{1}{4} \int_{-\infty}^\infty d\omega \omega \cos(u\omega) \coth(\beta\hbar\omega/2) - \\
&\quad \frac{1}{2} \int_0^\infty d\omega \omega \cos(u\omega) \\
&= -\frac{1}{2} \left(\frac{\pi}{\beta\hbar} \right)^2 \operatorname{cosech}^2\left(\frac{\pi u}{\beta\hbar}\right) + \frac{1}{2} \mathcal{P} \frac{1}{u^2}.
\end{aligned} \tag{35}$$

Notice that the value of this last integral is independent of the integration path around the origin, $\omega = 0$, because the residue at that point is zero.

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Figure Captions

Figure 1. Plot of the monotonic increasing function $G(v_0)$. Numerical analysis shows that $G(v_V) = 0$ for $v_V = 1.763876988$ and $G(v_E) = -1$ for $v_E = 0.64889408$ (with ten significant figures).

Figure 2. Dimensionless thermodynamic potentials S/k_B , $\Delta S/k_B$, $\Delta f = \pi a_1 \Delta F/\hbar c$, and $\Delta u = \pi a_1 \Delta E/\hbar c$ as functions of the dimensionless variable $\xi = \pi k_B T a_1 / \hbar c$. Three particular configurations are shown: $a_2 = a_3 = 100a_1$ (pizza box), $a_1 = a_2 = a_3$ (cube), and $a_2 = a_3 = a_1/10$ (wave guide), in the first, second and third columns respectively. The total entropy is given in the first row; notice that it is always positive, which is not the case for the difference between the entropy in “free space” and its finite domain value, as seen in the second row . The finite domain free and internal energies are shown in the third and fourth rows respectively. In all cases, the finite domain thermodynamic potentials have the physically expected values as $\pi k_B T a_1 / \hbar c \rightarrow 0$, and tend to zero as $\pi k_B T a_1 / \hbar c \rightarrow \infty$.

Figure 3. Dimensionless pressures on the walls 1 and 3, $p_1 = \pi a_1^4 P_1 / \hbar c$ and $p_3 = \pi a_1^4 P_3 / \hbar c$ as function of the dimensionless variable $\xi = \pi k_B T a_1 / \hbar c$ for a “pizza box” configuration (upper panel), and a “waveguide” configuration (lower panel). For comparison the pressures corresponding to F_{BB} are plotted in dotted lines.



